Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Structure, Melting and Dynamics of Screened Coulomb Systems in 2D—Role of Substrate Corrugation

S. D. Mahanti [a], H. Seong [a], S. Sen [a] & T. Cagin [a b]

[a] Department of Physics and Astronomy & Center for Fundamental Materials Research, Michigan State University, East Lansing, MI, 48824-1116, U.S.A.

[b] Molecular Simulations Inc., Suite 540, S. Robles Avenue, CA, 91101, U.S.A.

Version of record first published: 23 Oct 2006.

To cite this article: S. D. Mahanti , H. Seong , S. Sen & T. Cagin (1994): Structure, Melting and Dynamics of Screened Coulomb Systems in 2D—Role of Substrate Corrugation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 141-146

To link to this article: http://dx.doi.org/10.1080/10587259408051679

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 141–146
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

STRUCTURE, MELTING AND DYNAMICS OF SCREENED COULOMB SYSTEMS IN 2D—ROLE OF SUBSTRATE CORRUGATION†

S. D. MAHANTI, H. SEONG, S. SEN, & T. CAGIN*
Department of Physics and Astronomy & Center for Fundamental Materials Research, Michigan State University, East Lansing, MI 48824-1116. U.S.A.
*Molecular Simulations Inc., Suite 540, S. Robles Avenue, CA 91101. U.S.A.

Abstract Physical properties of a large class of intercalation compounds can be modeled by a two-dimensional (2D) repulsive screened Coulomb system subjected to a substrate corrugation potential. Using molecular dynamics simulation, we have investigated structural, thermodynamic (mainly 2D melting), and dynamic properties of these systems for different intercalant concentrations and corrugated strengths. For parameters appropriate to RbC_{24}, a stage-2 graphite intercalation compound (GIC), we obtain an incommensurate ground state structure consisting of nano domains of $\sqrt{7} \times \sqrt{7}$ triangular plaquettes separated by thick domain walls. A small decrease in the density gives a commensurate periodic domain wall ground state. In contrast to the corrugation-free systems, melting in these systems is continuous. Dynamics in the presence of corrugation show characteristics of a marginal fluid where solid and fluid–like dynamics coexist.

I. INTRODUCTION

X-ray[1], quasi-elastic neutron[2], and inelastic neutron[3] scattering studies in high-stage alkali metal GICs have provided a detailed understanding of the physical properties of 2D repulsive screened Coulomb (RSC) systems in the presence of an external periodic potential. In addition, Monte Carlo[4] and molecular dynamics (MD)[5-6] simulation studies of realistic models have added a great deal more to our current understanding of these systems. Some of the remarkable characteristics of the high-stage alkali GICs are: (1) a rich variety of ground state structures (of the alkali intercalants) consisting of nanodomains and domain walls of comparable size, (2) a continuous transition from a domain-wall solid to a lattice-liquid, and (3) observation of the coexistence of solid-like and liquid-like dynamics above the solid-liquid transition temperature. All these characteristics are governed primarily by the strong corrugation potential caused by the host graphene layers.

In spite of considerable experimental and theoretical effort in the area of GICs, one still does not have a complete understanding of the 2D-RSC systems because one can

not at will tune the planar intercalant density (ρ) and the strength of the corrugation potential (K). Therefore, to have a broader understanding of the physical properties of 2D-RSC systems in the (ρ, K,T) space, where T is the temperature, we have carried out extensive MD simulations[7-9] in these systems. In this paper, we summarize some of our results focusing on three specific questions: (1) Can realistic potential models (both single-and inter-particle) give an adequate description of the domain-wall solid and how the ground state structure changes with ρ? (2) What is the nature of the melting transition and how does it depend on K and ρ? and (3) How do the dynamics of a homogeneous fluid evolve to that of a lattice-fluid as we increase K? For comparing our MD results with experiment we have chosen, whenever possible, parameters appropriate for the stage-2 RbC_{24} because an excellent model for the one particle potential is available for this system.[1]

II. MODEL AND SYSTEMS

The model consists of *Rb* ions interacting through a repulsive screened Coulomb potential and moving in 2D. The effects of graphene and other intercalant layers is represented by a potential V_1, where

$$V_1(r) = -2K\left[2\cos(2\pi x/a)\cos\left(2\pi y/\sqrt{3}a\right) + \cos\left(4\pi y/\sqrt{3}a\right)\right]. \quad (1)$$

In Eq. (1), 2K is the strength of the corrugation potential measured in units of 300°K (in units of k_B) and a=2.46Å, is the graphite in-plane lattice constant. The two particle potential V_2 is given by,

$$V_2(r_{ij}) = q^2 \sum_{\langle ij \rangle} \exp\left(-\Gamma r_{ij}\right)/r_{ij} \quad (2)$$

where q is the charge on the *Rb* ions and Γ is the screening parameter. In the present study q = |e|, Γ= 0.49 $Å^{-1}$. For structure and melting studies we have chosen three systems: System I corresponds to RbC_{24} (ρ=0.0318 *Rb*/$Å^2$) without corrugation (2K = 0); System II has the same ρ as I, but 2K=0.9; System III has same K as II, but ρ = 0.0311 *Rb* ions/$Å^2$ corresponding to stage-2 $RbC_{24.57}$. For the dynamics studies we have chosen a series of systems with same density as I, but changing 2K from 0 to 0.9 in small intervals. For details of our MD simulations, see references 7-9.

III. GROUND STATE STRUCTURE

The angular averaged pair distribution function g(r) at 3°K for the system I shows the usual characteristics of a triangular lattice with the first peak at r = 2.45 (in units of a) corresponding to six nearest neighbors. In system II, this "near neighbor" structure is characterized by three distinct peaks at r = 2.19, 2.53, and 2.97. This clearly shows the profound influence of the corrugation potential on the intercalant structure in RbC_{24}. The static structure factor S(k) shows two observable peaks, I1 and I2, and their six rotational counterparts[7] whose positions agree very well with experiment.[10,1] To visualize the incommensurate ground state structure, we give in Fig. 1a, the positions of *Rb* ions. We see placquettes of $(\sqrt{7} \times \sqrt{7})$ triangular lattice consisting of 7 ions separated by domain walls of width 2 (in units of a). The domain walls are rather thick and due to the density constraint several plaquettes tend to fuse. If the ground state consisted of a periodic arrangement of these triangular plaquettes and separated by $(2 \times 3 \times \sqrt{7})$ domain walls, then the system would have corresponded to $RbC_{24.57}$. To see whether the ground state of this system (III) is indeed a periodic domain wall (PDW) solid, we have cooled it from a high temperature (so that we do not bias the structure) to 3°K, and the atomic arrangements are given in Fig. 1b. We clearly see a perfect PDW solid. The ground states obtained through MD are very close to that given by Zabel et al.,[1,10] although we have a more detailed understanding of the structure. The incommensurate ground state of RbC_{24} comes very close to be described by a PDW solid with a few local defects consisting of fused triangular plaquettes and dense domain wall regions.

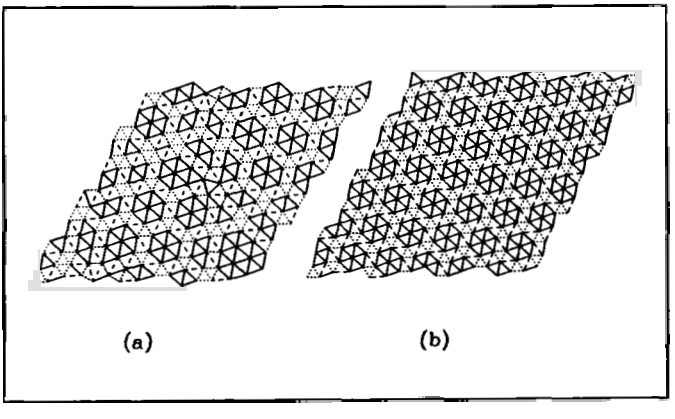

FIGURE 1. Low temperature solid structure for (a) system II (RbC_{24}) and (b) system III ($RbC_{24.57}$). The atoms are at the vertices and the solid, dotted, and dashed lines correspond to different near neighbor bond lengths.

IV. MELTING

Melting of 2D solids continues to be of great interest since the original two-stage dislocation and disclination unbinding transition ideas were put forward[11]. Although high-stage GICs can be approximated as 2D as regards their melting transition the effect of substrate corrugation can be significant.[8] To see this effect in RbC_{24}, we have monitored the temperature dependence of bond orientational order parameter[11] ψ_6 defined by

$$\psi_6 = \frac{1}{N}\left|\sum_{\ell j}\frac{1}{n_\ell}e^{i6\vartheta_{\ell j}}\right| \tag{3}$$

where the sum on l is over all N atoms, the sum on j is over the nearest neighbors of the atom l, and n_l is the number of such neighbors as defined by Voronoi polyhedra construction. The angle θ_{lj} is the orientation of the (lj) bond with respect to a fixed axis. In Fig. 2 (left panel) we give the T dependence of ψ_6 for systems I and II and in the right panel for the systems II and III. The nearly first-order transition seen in I becomes continuous in II, and III[8] in accord with the experimental observation in RbC_{24}.[1] The

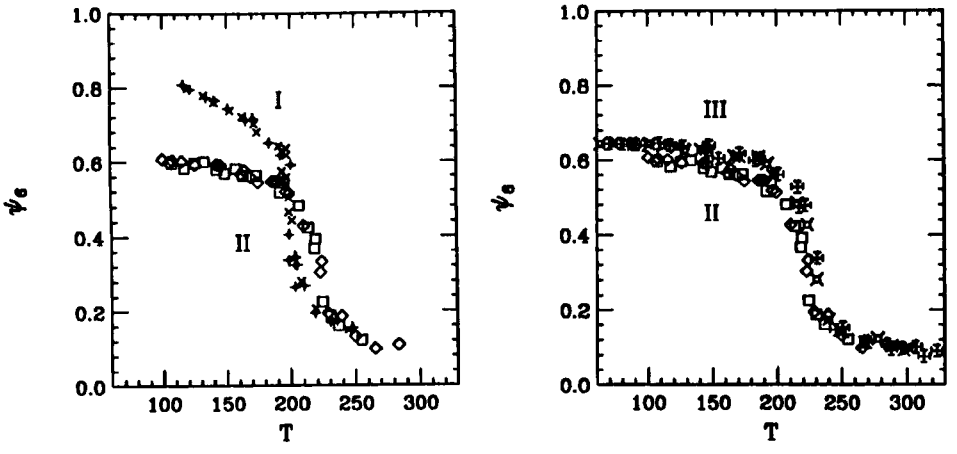

FIGURE 2. (left panel) Temperature dependence of the bond orientational order parameter for systems I and II, and (right panel) for systems II and III.

transition temperature in II is about 220°K, compared to experimental value of 165°K, the difference is perhaps due to the choice of the screening parameter Γ in our simulation. Systems II and III show almost similar melting behavior with the latter (whose ground state is a commensurate PDW solid) showing a slightly sharper

transition. We[8] find that the order parameter susceptibility χ_6 shows a dramatic drop at the transition temperature T_c in I, whereas in II and III, it peaks at a temperature higher than T_c and changes rather smoothly near T_c. This feature may be a general characteristics of the melting of a domain wall solid.

V. DYNAMICS IN THE FLUID PHASE

The incoherent (or self) dynamic structure factor $S_s(q,\nu)$ describes the single-particle dynamics of a fluid. A distinct advantage of MD over experiment is that it is straightforward to obtain $S_s(q,\nu)$ for all q whereas small q regions are difficult to access in experiment for coherent scatterers. In Fig. 3, we give $S_s(q,\nu)$ vs ν for different values of q for systems I and II. The main effect of corrugation is to narrow the width of the Lorentzian at small q (indicating the slowing down of diffusion) and change the spectrum at large q from a Gaussian (free particle response) to one with a broad finite frequency peak and a non-Lorentzian central peak. The latter has been interpreted as a signature of the coexistence of solid and liquid like behavior[2,3,5] which is a characteristic of a marginal fluid.[9]

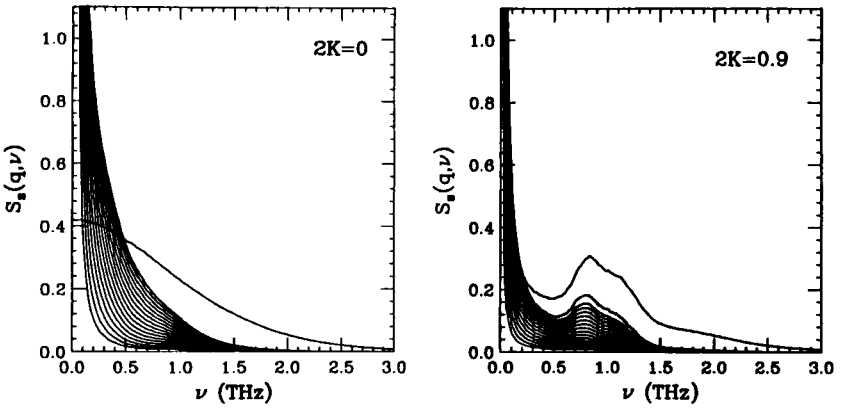

FIGURE 3. Incoherent dynamic structure factor $S_s(q,\nu)$ for system I (left panel), and for system II (right panel), for different values of q from 0.1 to 2.0, increasing in steps of 0.1. The uppermost curve corresponds to q=4; q is in unit of $Å^{-1}$.

To see how $S_s(q,\nu)$ evolves from that for a homogeneous fluid (2K=0) to a lattice-fluid (2K=0.9), we increase 2K, keeping q fixed at 4.0 and 0.4 and T at 250°K.[9] For large q, we find that the Gaussian evolves by changing the spectrum at all frequency scales. A central peak appears when $k_BT \geq \Delta$, the single particle barrier height. For

small q, one can clearly see a gradual narrowing indicating the slowing down of the diffusive process.

VI. SUMMARY AND CONCLUDING REMARKS

In summary, we see that MD simulation has contributed significantly to our understanding of the structure, melting, and dynamics of 2D RSC systems in the presence of a tunable corrugation potential. The ground state can be described as a domain wall solid where the domains and domain walls are of comparable size. Melting of these solids is continuous and is characterized by a peak in the bond orientational susceptibility χ_6 above the transition temperature. Above the melting transition, the dynamics is that of a marginal fluid where both solid and liquid dynamics coexist. With either increase in T or decrease in 2K, the dynamics change smoothly to that of an ordinary fluid.

†Supported by the Center for Fundamental Materials Research at Michigan State University, and NSF Grant #90-24955.

REFERENCES

1. S.C. Moss and R. Moret, Graphite Intercalation Compounds Vol I: Structure and Dynamics, ed. by H. Zabel and S. A. Solin (Springer Series in Material Science: V14, Berlin, 1990). p. 5.
2. A. Magerl, Graphite Intercalation Compounds Vol I: Structure and Dynamics, ed. by H. Zabel and S. A. Solin (Springer Series in Material Science: V14, Berlin, 1990). p. 221.
3. H. Zabel, Graphite Intercalation Compounds Vol I: Structure and Dynamics, ed. by H. Zabel and S. A. Solin (Springer Series in Material Science: V14, Berlin, 1990). p. 101.
4. M. Plischke and W.D. Leckie, Can. J. Phys. 60, 1139 (1982).
5 J.D. Fan, G. Reiter, and S.C. Moss, Phys. Rev. Lett., 64, 188 (1990).
6. Z. Chen, O.A. Karim, and B.M. Pettitt, J. Chem. Phys., 89, 1042 (1988).
7. H. Seong, S.D. Mahanti, T. Cagin, and S. Sen, Phys. Rev. B, 45, 8841 (1992).
8. H. Seong, S.D. Mahanti, S. Sen, and T. Cagin, Phys. Rev. B, 46, 8748, (1992).
9. H. Seong and S.D. Mahanti (unpublished); H. Seong, Ph.D. thesis, Michigan State University, East Lansing, MI (1993).
10. H. Zabel, et al., Phys. Rev. Lett., 57, 2041 (1986); see also, R. Clarke, et al., Phys. Rev. Lett., 47, 1407 (1981); see also, Ref. 1.
11. K. J. Strandburg, Rev. Mod. Phys., 60, 161 (1988).